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U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NUMBER

TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371

29610/CDT087A

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR

09/913381

INTERNATIONAL APPLICATION NO.
PCT/GB00/00476INTERNATIONAL FILING DATE
14 February 2000PRIORITY DATE CLAIMED
12 February 1999

TITLE OF INVENTION
OPTO-ELECTRICAL DEVICES

APPLICANT(S) FOR DO/EO/US

Jeremy H. BURROUGHES; Julian C. CARTER; Alec G. GUNNER; Stephen K. HEEKS; and Ian S. MILLARD

Applicant hereby submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (24) indicated below.
4. ☒ The US has been elected by the expiration of 19 months from the priority date (Article 31).
5. ☒ A copy of the International Application as filed (35 U.S.C. 371 (c) (2))
 - a. ☐ is attached hereto (required only if not communicated by the International Bureau).
 - b. ☒ has been communicated by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☐ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
 - a. ☐ is attached hereto.
 - b. ☐ has been previously submitted under 35 U.S.C. 154(d)(4).
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3))
 - a. ☐ are attached hereto (required only if not communicated by the International Bureau)
 - b. ☐ have been communicated by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☒ have not been made and will not be made.
8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☐ An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)).
10. ☐ An English language translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).
11. ☒ A copy of the International Preliminary Examination Report (PCT/IPEA/409).
12. ☒ A copy of the International Search Report (PCT/ISA/210).

Items 13 to 20 below concern document(s) or information included:

13. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
14. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included
15. ☒ A **FIRST** preliminary amendment
16. ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
17. ☐ A substitute specification.
18. ☐ A change of power of attorney and/or address letter.
19. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.
20. ☐ A second copy of the published international application under 35 U.S.C. 154(d)(4).
21. ☐ A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4)
22. ☒ Certificate of Mailing by Express Mail
23. ☒ Other items or information:

Postal card receipt

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U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR 1.53) 09/913381		INTERNATIONAL APPLICATION NO PCT/GB00/00476	ATTORNEY'S DOCKET NUMBER 29610/CDT087A
<div>24. The following fees are submitted.</div> <div>BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)) :</div> <div><input type="checkbox"/> Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO \$1000.00</div> <div><input checked="" type="checkbox"/> International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO \$860.00</div> <div><input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO \$710.00</div> <div><input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4) \$690.00</div> <div><input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) \$100.00</div> <div>ENTER APPROPRIATE BASIC FEE AMOUNT =</div> <div><div>\$860.00</div><div>\$0.00</div></div>			

Surcharge of **\$130.00** for furnishing the oath or declaration later than months from the earliest claimed priority date (37 CFR 1.492 (e)).

☐ 20 ☐ 30

\$0.00

a. ☒ A check in the amount of **\$1,022.00** to cover the above fees is enclosed.

b. ☐ Please charge my Deposit Account No. _____ in the amount of _____ to cover the above fees. A duplicate copy of this sheet is enclosed.

c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. **13-2855** A duplicate copy of this sheet is enclosed.

d. ☐ Fees are to be charged to a credit card. **WARNING:** Information on this form may become public. **Credit card information should not be included on this form.** Provide credit card information and authorization on PTO-2038.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

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SIGNATURE

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NAME

28,491
REGISTRATION NUMBER

August 13, 2001
DATE

Paragraph beginning at page 5, line 1 has been amended as follows:

The work function of the material of the third layer is preferably greater than 4.0 eV. The higher work function material is suitably a metal or an oxide. The higher work function material and/or the third layer itself preferably has an electrical conductivity greater than $10^5 (\Omega \cdot \text{cm})^{-1}$. The higher work function material is preferably Al, Cu, Ag, Au or Pt; or an alloy of two or more of those metals; or an alloy of one or more of those metals together with another metal; or an oxide such as tin oxide or indium-tin oxide (ITO). The thickness of the third layer is preferably in the range from 1000 Å to 10000 Å, preferably in the range from 2000 Å to 6000 Å, and most preferably around 4000 Å.

Please insert a new paragraph beginning at page 7, following line 5 as follows:

--figure 1 shows a typical cross-sectional structure of a prior art organic light-emissive device;

Paragraph beginning at page 7, line 28 has been amended as follows:

To form the device of figure 2 a transparent layer of ITO to form the anode electrode 10 may first be deposited on a sheet of glass 14. The glass sheet could be a sheet of sodalime or borosilicate glass of a thickness of, for instance, 1mm. The thickness of the ITO coating is suitably around 100 to 150nm and the ITO suitably has a resistance of between 10 and 30 Ω/\square . ITO-coated glass substrates of this type are commercially available. As an alternative to glass, the sheet 14 could be formed of perspex. As an alternative to ITO, gold or TO could be used as the anode.

[illegible]

IN THE ABSTRACT:

Please add an abstract as set forth on the attached sheet.

IN THE CLAIMS:

4. (Amended) An opto-electrical device as claimed in claim 1, wherein the compound is a fluoride.

5. (Amended) An opto-electrical device as claimed in claim 2, wherein the metal is a group 1 or 2 metal.

7. (Amended) An opto-electrical device as claimed in claim 2, wherein the said one of the layers is the first layer.

8. (Amended) An opto-electrical device as claimed in claim 2, wherein the said one of the layers is the second layer.

16. (Amended) An opto-electrical device as claimed in claim 1, wherein the said material having a work function above 3.5 eV is aluminium, gold or indium-tin oxide.

17. (Amended) An opto-electrical device as claimed in claim 1, wherein the cathode is transparent.

18. (Amended) An opto-electrical device as claimed in claim 1, wherein the opto-electrically active region is light-emissive.

19. (Amended) An opto-electrical device as claimed in claim 1, wherein the opto-electrically active region comprises a light-emissive organic material.

22. (Amended) An opto-electrical device as claimed in claim 19, comprising a charge transport layer between the light-emissive organic material and one of the electrodes.

Please delete claims 24 and 25, without prejudice.

Please add new claims 26-31, as follows:

26. An opto-electrical device as claimed in claim 4, wherein the metal is a group 1 or 2 metal.

27. An opto-electrical device as claimed in claim 26, wherein the metal is lithium.

28. An opto-electrical device as claimed in claim 4, wherein the said one of the layers is the first layer.

29. An opto-electrical device as claimed in claim 4, wherein the said one of the layers is the second layer.

30. An opto-electrical device as claimed in claim 4, wherein the other of the first and second layers comprises a metal.

31. An opto-electrical device as claimed in claim 30, wherein the other of the first and second layers comprises a metal selected from the group consisting of Li, Ba, Mg, Ca, Ce, Cs, Eu, Rb, K, Y, Sm, Na, Sm, Sr, Tb and Yb.

[illegible]

The filing fee has been calculated based on the claims as amended above. No new matter has been added.

MARSHALL, GERSTEIN & BORUN

By James P. Zeller
James P. Zeller
Reg. No. 28,491

- 7 -

are commercially available. As an alternative to glass, the sheet 14 could be formed of perspex. As an alternative to ITO, gold or TO could be used as the anode.

Paragraph beginning at page 13, line 26 has been amended as follows:

[The applicant draws attention to the fact that the present] The invention may include any inventive feature or combination of features disclosed herein either implicitly or explicitly or any generalisation thereof, without limitation to the scope of any of the [present] claims. In view of the foregoing description it will be evident to a person skilled in the art that various modifications may be made within the scope of the invention.

IN THE CLAIMS:

Please amend claims 4, 5, 7-19, and 22 as follows:

4. (Amended) An opto-electrical device as claimed in [any preceding] claim 1, wherein the compound is a fluoride.
5. (Amended) An [opti-electrical] opto-electrical device as claimed in [any of claims] claim 2 [to 4], wherein the metal is a group 1 or 2 metal.
7. (Amended) An opto-electrical device as claimed in [any of claims] claim 2 [to 6], wherein the said one of the layers is the first layer.

[illegible]

15. (Amended) An opto-electrical device as claimed in [any preceding] claim 1, wherein the said material having a work function above 3.5 eV has an electrical conductivity greater than $10^5 [(*.cm)^{-1}] (\Omega.cm)^{-1}$.

16. (Amended) An opto-electrical device as claimed in [any preceding] claim 1, wherein the said material having a work function above 3.5 eV is aluminium, gold or indium-tin oxide.

17. (Amended) An opto-electrical device as claimed in [any preceding] claim 1, wherein the cathode is transparent.

18. (Amended) An opto-electrical device as claimed in [any preceding] claim 1, wherein the opto-electrically active region is light-emissive.

19. (Amended) An opto-electrical device as claimed in [any preceding] claim 1, wherein the opto-electrically active region comprises a light-emissive organic material.

22. (Amended) An opto-electrical device as claimed in [any of claims] claim 19 [to 21], comprising a charge transport layer between the light-emissive organic material and one of the electrodes.

Please delete claims 24 and 25, without prejudice.

Please add new claims 26-31, as follows:

26. An opto-electrical device as claimed in claim 4, wherein the metal is a group 1 or 2 metal.

27. An opto-electrical device as claimed in claim 26, wherein the metal is lithium.

28. An opto-electrical device as claimed in claim 4, wherein the said one of the layers is the first layer.

29. An opto-electrical device as claimed in claim 4, wherein the said one of the layers is the second layer.

30. An opto-electrical device as claimed in claim 4, wherein the other of the first and second layers comprises a metal.

31. An opto-electrical device as claimed in claim 30, wherein the other of the first and second layers comprises a metal selected from the group consisting of Li, Ba, Mg, Ca, Ce, Cs, Eu, Rb, K, Y, Sm, Na, Sm, Sr, Tb and Yb.

WO 00/48257

PCT/GB00/00476

OPTO-ELECTRICAL DEVICES

This invention relates to opto-electrical devices, for example devices for emitting or detecting light.

One specific class of opto-electrical devices is those that use an organic material for light emission or detection. Light-emissive organic materials are described in PCT/WO90/13148 and US 4,539,507, the contents of both of which are incorporated herein by reference. The basic structure of these devices is a light-emissive organic layer, for instance a film of a poly(p-phenylenevinylene ("PPV"), sandwiched between two electrodes. One of the electrodes (the cathode) injects negative charge carriers (electrons) and the other electrode (the anode) injects positive charge carriers (holes). The electrons and holes combine in the organic layer generating photons. In PCT/WO90/13148 the organic light-emissive material is a polymer. In US 4,539,507 the organic light-emissive material is of the class known as small molecule materials, such as (8-hydroxyquinoline)aluminium ("Alq3"). In a practical device one of the electrodes is typically transparent, to allow the photons to escape the device.

Figure 1 shows a typical cross-sectional structure of such an organic light-emissive device ("OLED"). The OLED is typically fabricated on a glass or plastic substrate 1 coated with a transparent material such as indium-tin-oxide ("ITO") to form an anode 2. Such coated substrates are commercially available. The ITO-coated substrate is covered with at least a thin film of an electroluminescent organic material 3 and a final cathode layer 4, which is typically a metal or alloy.

Some particularly attractive applications of such devices are as displays in battery-powered units such as portable computers and mobile phones. Therefore, to extend the battery life of such units, there is a particularly strong need to increase the efficiency of the light-emissive devices. One route to improving efficiency is by careful choice and design of the light-emissive material itself. Another is by

optimising the physical layout of the display. A third is by improving the conditions for charge injection into and charge recombination in the emissive layer.

To improve the conditions for charge injection into and charge recombination in the emissive layer it is known to include a charge transport layer of an organic material such as polystyrene sulphonic acid doped polyethylene dioxythiophene ("PEDOT-PSS") between one or both of the electrodes and the emissive layer. A suitably chosen charge transport layer can enhance charge injection into the emissive layer and resist reverse flow of charge carriers, which favours charge recombination. It is also known to form the electrodes from materials having work functions that aid the desired flow of charge carriers. For example, a low work function material such as calcium or lithium is preferred as the cathode. PCT/WO97/08919 discloses a cathode formed of a magnesium:lithium alloy.

According to one aspect of the present invention there is provided an opto-electrical device comprising: an anode electrode; a cathode electrode; and an opto-electrically active region located between the electrodes; the cathode electrode including: a first layer comprising a material having a work function below 3.5 eV; a second layer of a different composition from the first layer, comprising another material having a work function below 3.5 eV, the second layer being further from the opto-electrically active region than the first layer; and a third layer comprising a material having a work function above 3.5 eV, the third layer being further from the opto-electrically active region than the first layer..

According to a second aspect of the present invention there is provided a method for forming an opto-electrical device, the method comprising: depositing an anode electrode; depositing over the anode electrode a region of an opto-electrically active material; depositing over the region of opto-electrically active material a material having a work function below 3.5 eV to form a first cathode layer; depositing over the first cathode layer another material having a work function below 3.5 eV to form a second cathode layer of a different composition from the

first cathode layer; and depositing over the second cathode layer a material having a work function above 3.5 eV to form a third cathode layer.

The first layer may be adjacent to the opto-electrically active region or there may be one or more other layers (preferably electrically conductive layers) between the first layer and the opto-electrically active region. The opto-electrically active region is suitably in the form of a layer, preferably a layer of an opto-electrically active material. The opto-electrically active region is suitably active to emit light or to generate an electrical field in response to incident light. The device is preferably an electroluminescent device.

The thickness of the first layer is suitably less than 50 Å, optionally less than 30 Å, or less than 25 Å or 20 Å. The thickness of the first layer could be less than 15 Å or 10 Å. The thickness of the first layer may be in the range from 5 Å to 20 Å, possibly around 15 Å. More generally, it is preferred that the thickness of the first layer is in the range from 10 Å to 140 Å. The first layer is preferably, but not necessarily thinner than the second layer.

The thickness of the second layer is suitably less than 1000 Å, and preferably less than 500 Å. The thickness of the second layer is suitably more than 40 Å or 100 Å, and optionally more than 150 Å or 200 Å. The thickness of the second layer is preferably in the range from 40 Å to 500 Å.

The said material having a work function below 3.5 eV of which the first layer is comprised ("the first low work function material") preferably has a higher work function than the said material having a work function below 3.5 eV of which the second layer is comprised ("the second low work function material"), or could alternatively have a lower work function than it. The work functions of the materials as referred to herein are preferably their effective work functions in the device, which may be different from their bulk work functions. Thus the first low work function material preferably has an effective work function in the device of

less than 3.5eV and/or the second low work function material preferably has an effective work function in the device of less than 3.5 eV.

One of the first and second low work function materials is preferably a compound or complex of a group 1, group 2 or transition metal. That material is preferably a compound - for example a halide (e.g. a fluoride), oxide, carbide or nitride). That material is preferably a compound of a metal such as Mg, Li, Cs or Y.

The second low work function material may be a metal selected from the following list: Li, Ba, Mg, Ca, Ce, Cs, Eu, Rb, K, Sm, Y, Na, Sr, Tb or Yb; or an alloy of two or more of such metals; or an alloy of one or more of such metals together with another metal such as Al, Zr, Si, Sb, Sn, Zn, Mn, Ti, Cu, Co, W, Pb, In or Ag.

The first and second low work function materials are preferably different materials. In one preferred embodiment the first low work function material is calcium and the second low work function material is lithium fluoride. In another preferred embodiment the second low work function material is calcium and the first low work function material is lithium fluoride

The first low work function material suitably has a (effective) work function less than 3.4 eV, or less than 3.3 eV or less than 3.2 eV, or less than 3.2 eV or less than 3.1 eV or less than 3.0 eV. The second low work function material suitably has a (effective) work function less than 3.4 eV, or less than 3.3 eV or less than 3.2 eV, or less than 3.2 eV or less than 3.1 eV or less than 3.0 eV.

The first low work function material preferably does not cause significant degradation of the material of the active region when the two are in contact. The second low work function material may be a material that is capable of causing degradation of the material of the active region when the two are in contact. The first low work function material may, when in contact with the material of the active region, form an intermediate state between those of the material of the active region and those of the second layer.

The work function of the material of the third layer is preferably greater than 4.0 eV. The higher work function material is suitably a metal or an oxide. The higher work function material and/or the third layer itself preferably has an electrical conductivity greater than $10^5 \text{ (}\Omega\text{.cm)}^{-1}$. The higher work function material is preferably Al, Cu, Ag, Au or Pt; or an alloy of two or more of those metals; or an alloy of one or more of those metals together with another metal; or an oxide such as tin oxide or indium-tin oxide (ITO). The thickness of the third layer is preferably in the range from 1000 Å to 10000 Å, preferably in the range from 2000 Å to 6000 Å, and most preferably around 4000 Å.

Suitably more than 50%, more than 80%, more than 90% or more then 95% of the first layer consists of the first low work function material. Preferably the first layer substantially wholly comprises the first low work function material. Most preferably the first layer consists of the first low work function material together with any impurities. Suitably more than 50%, more than 80%, more than 90% or more then 95% of the second layer consists of the second low work function material. Preferably the second layer substantially wholly comprises the second low work function material. Most preferably the second layer consists of the second low work function material together with any impurities. Suitably more than 50%, more than 80%, more than 90% or more then 95% of the third layer consists of the higher work function material. The third layer preferably substantially wholly comprises the higher work function material. Most preferably the third layer consists of the higher work function material together with any impurities.

The second layer is preferably adjacent to the first layer. The third layer is preferably adjacent to the second layer. Alternatively, the cathode may comprise further layers located between the first, second and/or third layers. The cathode is preferably inorganic, most preferably metallic.

One of the electrodes is preferably light-transmissive, and most preferably transparent. This is preferably but not necessarily the anode electrode, which could be formed of tin oxide (TO), indium-tin oxide (ITO) or gold.

The opto-electrically active region may be light-emissive or (suitably on the application of a suitable electric field across it) or may be light-sensitive (suitably generating an electric field in response to incident light). The opto-electrically active region suitably comprises a light-emissive material or a light-sensitive material. Such a light-emissive material is suitably an organic material and preferably a polymer material. The light-emissive material is preferably a semiconductive and/or conjugated polymer material. Alternatively the light-emissive material could be of other types, for example sublimed small molecule films or inorganic light-emissive material. The or each organic light-emissive material may comprise one or more individual organic materials, suitably polymers, preferably fully or partially conjugated polymers. Example materials include one or more of the following in any combination: poly(p-phenylenevinylene) ("PPV"), poly(2-methoxy-5(2'-ethyl)hexyloxyphenylenevinylene) ("MEH-PPV"), one or more PPV-derivatives (e.g. di-alkoxy or di-alkyl derivatives), polyfluorenes and/or co-polymers incorporating polyfluorene segments, PPVs and related co-polymers, poly(2,7-(9,9-di-n-octylfluorene)-(1,4-phenylene-((4-secbutylphenyl)imino)-1,4-phenylene)) ("TFB"), poly(2,7-(9,9-di-n-octylfluorene) - (1,4-phenylene-((4-methylphenyl)imino)-1,4-phenylene-((4-methylphenyl)imino) - 1,4-phenylene)) ("PFM"), poly(2,7 - (9,9 - di-n-octylfluorene) - (1,4-phenylene-((4-methoxyphenyl)imino)-1,4-phenylene-((4-methoxyphenyl)imino)-1,4-phenylene)) ("PFMO"), poly (2,7-(9,9-di-n-octylfluorene) ("F8") or (2,7-(9,9-di-n-octylfluorene)-3,6-Benzothiadiazole) ("F8BT"). Alternative materials include small molecule materials such as Alq3.

There may be one or more other layers in the device. There may be one or more charge transport layers (preferably of more or more organic materials) between the active region and one or other of the electrodes. The or each charge transport layer may suitably comprise one or more polymers such as polystyrene sulphonic

acid doped polyethylene dioxythiophene ("PEDOT-PSS"), poly(2,7-(9,9-di-n-octylfluorene)-(1,4-phenylene-(4-imino(benzoic acid))-1,4-phenylene-(4-imino(benzoic acid))-1,4-phenylene)) ("BFA"), polyaniline and PPV.

The present invention will now be described by way of example with reference to the accompanying drawings, in which:

figure 2 is a cross-section of a light-emissive device;

figures 3 to 4 show data on the performance of several light-emissive devices; and

figures 5 and 6 show experimental data for a set of devices having cathodes of different compositions;

figure 7 shows experimental data for a set of devices having cathodes of different configurations; and

figures 8 and 9 show experimental data for devices having cathode layers of different thicknesses.

The illustrated thicknesses of the layers in figure 2 are not to scale.

The device of figure 2 comprises an anode electrode 10 and a cathode electrode 11. Located between the electrode layers is an active layer 12 of light-emissive material. A charge transport layer 13 of PEDOT:PSS is located between the anode electrode 10 and the light-emissive layer 12. The device is formed on a glass substrate 14.

The metallic cathode 11 comprises three layers. Next to the emissive layer 12 is a first layer 15, of calcium. Over that is a second layer 16, of lithium. Over that is a third layer 17, of aluminium. As will be described below, this structure has been found to provide a significant increase in device efficiency.

To form the device of figure 2 a transparent layer of ITO to form the anode electrode 10 may first be deposited on a sheet of glass 14. The glass sheet could be a sheet of sodalime or borosilicate glass of a thickness of, for instance, 1mm. The thickness of the ITO coating is suitably around 100 to 150nm and the ITO

suitably has a sheet resistance of between 10 and 30 Ω/\square . ITO-coated glass substrates of this type are commercially available. As an alternative to glass, the sheet 14 could be formed of perspex. As an alternative to ITO, gold or TO could be used as the anode.

Over the ITO anode is deposited a hole transport or injecting layer 13. The hole transport layer is formed from a solution containing PEDOT:PSS with a ratio of PEDOT to PSS of around 1 to 5.5. The thickness of the hole transport layer is suitably around 500 Å. The hole transport layer is spin-coated from solution and then baked at around 200°C for 1 hour in a nitrogen environment.

Then the electroluminescent layer 15 is deposited. In this example, the electroluminescent layer is formed of 20% TFB in 5BTF8. The term 5BTF8 refers to poly (2,7-(9,9-di-*n*-octylfluorene) ("F8") doped with 5% poly-(2,7-(9,9-di-*n*-octylfluorene)-3,6-benzothiadiazole) ("F8BT"). the term TFB refers to poly(2,7-(9,9-di-*n*-octylfluorene)-(1,4-phenylene-((4-secbutylphenyl)imino)-1,4-phenylene)). This mixture is coated over the hole transport layer by spin-coating typically to a thickness of around 750 Å. Other materials such as PPV could be used for the emissive layer. The emissive layer could be formed by other routes such as blade or meniscus coating and could be deposited in precursor form if desired.

The cathode is then deposited. The three distinct layers of the cathode are deposited by successive thermal evaporation steps *in vacuo* at a base pressure of less than 10^{-8} mbar. Preferably the vacuum is not broken between the successive steps, to reduce the possibility of contamination of the interfaces between the layers. One alternative to thermal evaporation is sputtering, but this is less preferred for at least the deposition of the layer 15 adjacent to the emissive layer since it may cause damage to the emissive layer 12. In the first thermal evaporation step the layer 15 is deposited. The layer 15 is of calcium and has a thickness of approximately 5 to 25 Å, preferably around 15 Å. In the second thermal evaporation step the layer 16 is deposited. The layer 16 is of lithium and has a thickness of around 100 to 500 Å. In the third thermal evaporation step the

layer 17 is deposited. The layer 17 is of aluminium and has a thickness of around 4000 Å.

Finally, contacts are attached to the layers 10 and 17 and, although the aluminium layer 16 may act to some extent as an encapsulant, the device is preferably sealed in epoxy resin for environmental protection.

In use, when a suitable voltage is applied between the anode and the cathode the light-emissive layer is stimulated to emit light. This passes to a viewer through the transparent anode and the glass cover sheet.

The applicant has found that a device of this type has significantly increased efficiency. Figures 3 to 4 show data for the performance of devices of a similar device to that of figure 2 (devices E to H) and two comparative device designs (devices A to D and devices J to P).

The common structures of the devices were as follows:

- Substrate: glass
- Anode: ITO
- Charge transport layer: 1:5.5 PEDOT:PSS; thickness 500 Å
- Emissive layer: 4:1 5BTF8:TFB; thickness 750 Å

The cathodes of the devices were as follows:

Devices A to D:

- calcium layer of thickness 500 Å adjacent to emissive layer; and
- capping layer of aluminium of thickness 4000 Å.

Devices E to H:

- lithium layer of thickness 500 Å adjacent to emissive layer; then
- calcium layer of thickness 1000 Å; and
- capping layer of aluminium of thickness 4000 Å.

Devices J to P:

- lithium layer of thickness 25 Å adjacent to emissive layer; and

- capping layer of aluminium of thickness 4000 Å.

Figure 3 shows the peak measured efficiencies of the devices in Lm/W and Cd/A. Figure 4 shows the drive voltages for the devices at brightnesses of 0.01, 100 and 1000 Cd/m². Figure 3 shows that the peak efficiency of devices E to H is markedly greater than those of the other devices. Figure 4 shows that devices E to H do not suffer any significant increase in drive voltage, and have significantly lower drive voltages than devices J to P.

Figures 5 to 9 show data for further similar devices. Figure 5 shows experimental data for devices comprising an ITO anode, an 80nm layer of PEDOT:PSS, a 63nm layer of a blue emissive material (spin-coated in a glovebox) and a cathode formed of a first layer next to the emissive layer of a composition as indicated against the respective plot, a second 10nm layer of Ca and a final layer of Al. Figure 6 shows experimental data for devices comprising an ITO anode, an 80nm layer of PEDOT:PSS, a 70nm layer of a green emissive material (F8:TFB:F8BT spin-coated in a glovebox) and a cathode formed of a first layer next to the emissive layer of a composition as indicated against the respective plot, a second 10nm layer of Ca and a final layer of Al. The experimental data are: electroluminescence spectra, luminous efficiency against voltage, current density against voltage, brightness against voltage and brightness against time. The efficiency data are summarised as follows:

Material of first cathode layer	Blue: maximum Lm/W	Green: maximum Lm/W
MgF ₂	0.30	8.5
MgI ₂	0.01	0.12
LiF	2.0	15
LiCl	0.18	10
LiBr	0.05	12
LiI	0.35	13
CsCl	0.60	0.9

CsBr	0.75	4.5
CsI	0.80	8.0
YF	1.25	14
CaAl	0.73	16

The EL spectra of the blue emitters were only slightly dependant on the cathode materials used, those with higher current densities showing the typical aggregate feature. Green spectra were relatively independent of the cathode materials used. The device performance appeared to be principally dependant on the metal constituent of the first cathode layer. The Mg-based devices had the worst performance for both emissive polymers, with relatively low efficiencies and currents. Cs-based devices had intermediate performance. LiF gave the highest performing devices. Other Li halides had relatively poor performance for blue emission and variable efficiency for green.

Figure 7 shows efficiency data for similar devices having ITO anodes, a PEDOT:PSS layer, an emissive layer capable of emitting blue, green or red light (as indicated on the respective plot) and electrodes of:

- (a) a Ca layer adjacent to the emitter and an upper layer of Al;
- (b) a LiF layer (6nm thick) adjacent to the emitter, then a layer of Ca (10nm thick) and an upper layer of Al;
- (c) a Ca layer (5nm thick) adjacent to the emitter, then a layer of LiF (6nm thick) and an upper layer of Al.

Figure 8 shows efficiency data as a plot of maximum Lm/W for similar blue, green and red devices having a range of thicknesses for the LiF layer in the Ca/LiF/Al configuration. Figure 9 shows efficiency data as a plot of maximum Lm/W for devices having a range of thicknesses for the LiF layer in the LiF/Ca/Al configuration.

The applicant has also obtained advantageous results by replacing the Ca layer in such devices with a similar layer of Yb or Ba. Other materials such as Sm, Y and Mg would be expected to yield similar results.

Most of the above devices include in their cathodes a layer of a group 1 or group 2 metal halide, such as LiF. Other group 1 and 2 metal compounds and complexes, such as LiO have been investigated by the applicant and found to give advantageous results. Transition metal halides, compounds and complexes, such as YF (see above) may also give advantageous results. Organic complexes of group 1, group 2 or transition metals may also give advantageous results. These materials include materials that may potentially operate by providing a barrier effect (e.g. LiO) or by another effect due to their low effective work function in this situation (e.g. LiF).

It is believed that, when the layer 15 of the cathode that is adjacent to the emissive layer 12 is sufficiently thin that the properties of the overlying cathode layer 16 can influence charge injection from the cathode into the emissive layer, there is an opportunity to select materials for the layers 15 and 16 such that by a combination of their properties the performance of the device can be enhanced. Possible mechanisms for this enhancement are believed to include: (a) prevention by the layer 15 of adverse interactions between organic layer(s) of the device (e.g. layer 15) and the material of the layer 16, whilst retaining at least some of the injection properties of the material of the layer 16; and (b) the formation by the layer 15 (e.g. with organic layer(s) such as layer 15) of intermediate states that aid electron injection from the layer 16. The layer 15 should be sufficiently thin to allow the effect to occur but sufficiently thick that it can be deposited reproducibly and uniformly (without excessive defects). To exploit possible mechanism (a) the layer 16 could be formed from a material that is more reactive than that of layer 15, but has a lower work function. It should also be noted that highly advantageous performance is also obtained when a layer of a suitable material (e.g. LiF) is spaced slightly from the emissive material, as in the Ca/LiF/Al devices of figures 7 and 8. In general, possible mechanisms include surface induced dipoles, modified work functions, charge transfer formation of chemically stable compounds and dissociation of the compound layer of the cathode to form a doped injection layer.

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present claims. In view of the foregoing description it will be evident to a person skilled in the art that various modifications may be made within the scope of the invention.

CLAIMS

1. An opto-electrical device comprising:
 - an anode electrode;
 - a cathode electrode; and
 - an opto-electrically active region located between the electrodes;the cathode electrode including:
 - a first layer comprising a material having a work function below 3.5 eV;
 - a second layer of a different composition from the first layer, comprising another material having a work function below 3.5 eV, the second layer being further from the opto-electrically active region than the first layer; and
 - a third layer comprising a material having a work function above 3.5 eV, the third layer being further from the opto-electrically active region than the first layer.
2. An opto-electrical device as claimed in claim 1, wherein one of the first and second layers comprises a compound of a group 1 or group 2 or transition metal.
3. An opto-electrical device as claimed in claim 2, wherein the compound is a halide.
4. An opto-electrical device as claimed in any preceding claim, wherein the compound is a fluoride.
5. An opto-electrical device as claimed in any of claims 2 to 4, wherein the metal is a group 1 or 2 metal.
6. An opto-electrical device as claimed in claim 5, wherein the metal is lithium.
7. An opto-electrical device as claimed in any of claims 2 to 6, wherein the said one of the layers is the first layer.

8. An opto-electrical device as claimed in any of claims 2 to 6, wherein the said one of the layers is the second layer.

9. An opto-electrical device as claimed in any of claims 2 to 8, wherein the other of the first and second layers comprises a metal.

10. An opto-electrical device as claimed in claim 9, wherein the other of the first and second layers comprises a metal selected from the group comprising: Li, Ba, Mg, Ca, Ce, Cs, Eu, Rb, K, Y, Sm, Na, Sm, Sr, Tb or Yb.

11. An opto-electrical device as claimed in any preceding claim, wherein the second layer is thicker than the first layer.

12. An opto-electrical device as claimed in any preceding claim, wherein the thickness of the second layer is greater than 100 Å.

13. An opto-electrical device as claimed in any preceding claim, wherein the said material having a work function below 3.5 eV of which the first layer is comprised has a higher work function than the said material having a work function below 3.5 eV of which the second layer is comprised.

14. An opto-electrical device as claimed in any preceding claim, wherein the thickness of the third layer is greater than 1000 Å.

15. An opto-electrical device as claimed in any preceding claim, wherein the said material having a work function above 3.5eV has an electrical conductivity greater than $10^5 \text{ } (\Omega \cdot \text{cm})^{-1}$.

16. An opto-electrical device as claimed in any preceding claim, wherein the said material having a work function above 3.5eV is aluminium, gold or indium-tin oxide

17. An opto-electrical device as claimed in any preceding claim, wherein the cathode is transparent.
18. An opto-electrical device as claimed in any preceding claim, wherein the opto-electrically active region is light-emissive.
19. An opto-electrical device as claimed in any preceding claim, wherein the opto-electrically active region comprises a light-emissive organic material.
20. An opto-electrical device as claimed in claim 19, wherein the light-emissive organic material is a polymer material.
21. An opto-electrical device as claimed in claim 20, wherein the light-emissive organic material is a conjugated polymer material.
22. An opto-electrical device as claimed in any of claims 19 to 21, comprising a charge transport layer between the light-emissive organic material and one of the electrodes.
23. A method for forming an opto-electrical device, the method comprising:
 - depositing an anode electrode;
 - depositing over the anode electrode a region of an opto-electrically active material;
 - depositing over the region of opto-electrically active material a material having a work function below 3.5 eV to form a first cathode layer;
 - depositing over the first cathode layer another material having a work function below 3.5 eV to form a second cathode layer of a different composition from the first cathode layer; and
 - depositing over the second cathode layer a material having a work function above 3.5 eV to form a third cathode layer.

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24. An opto-electrical device substantially as herein described with reference to figures 2 to 9 of the accompanying drawings.

25. A method for forming an opto-electrical device substantially as herein described with reference to figures 2 to 9 of the accompanying drawings.

ABSTRACT

An opto-electrical device comprising an anode electrode, a cathode electrode, and an opto-electrically active region located between the electrodes, the cathode electrode including a first layer comprising a material having a work function below 3.5 eV, a second layer of a different composition from the first layer, comprising another material having a work function below 3.5 eV, the second layer being further from the opto-electrically active region than the first layer, and a third layer comprising a material having a work function above 3.5 eV, the third layer being further from the opto-electrically active region than the first layer.

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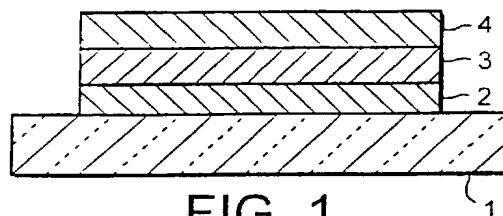


FIG. 1

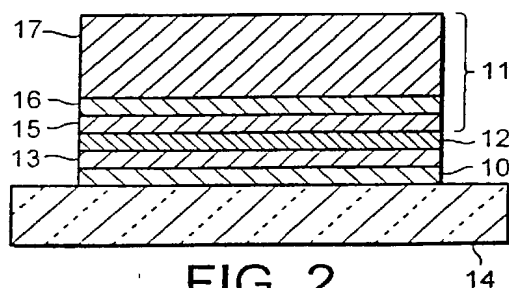


FIG. 2

DIFFERENT CATHODE LAYER STRUCTURE WITH Li/Ca/Al
 PEDOT=Ba/PEDT/6:Sp/PSS/1 (1:5.5 PEDT:PSS) 500Å
 EMITTER=R/5BTF8/1:R/TFB/1 (4:1) 750Å

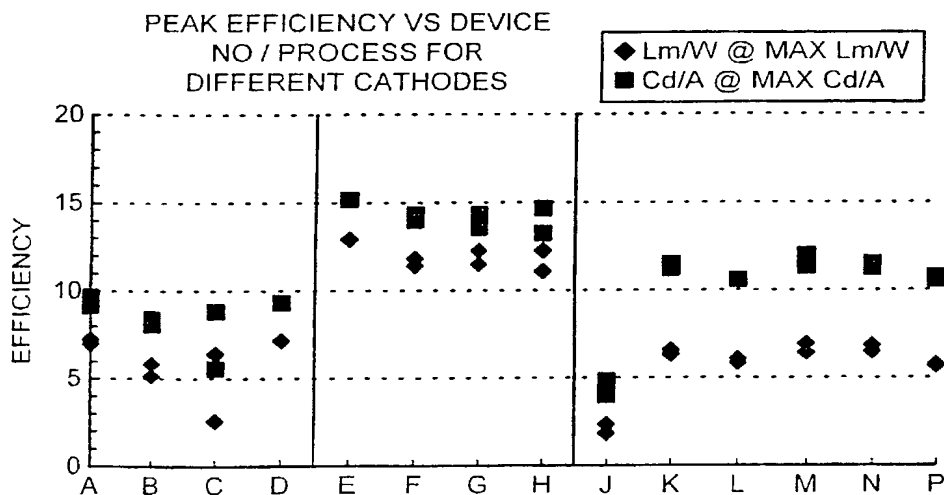


FIG. 3

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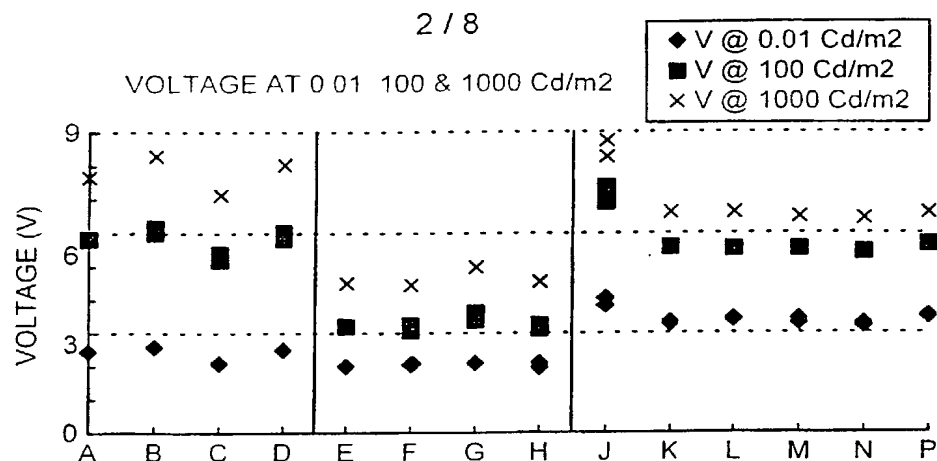


FIG. 4

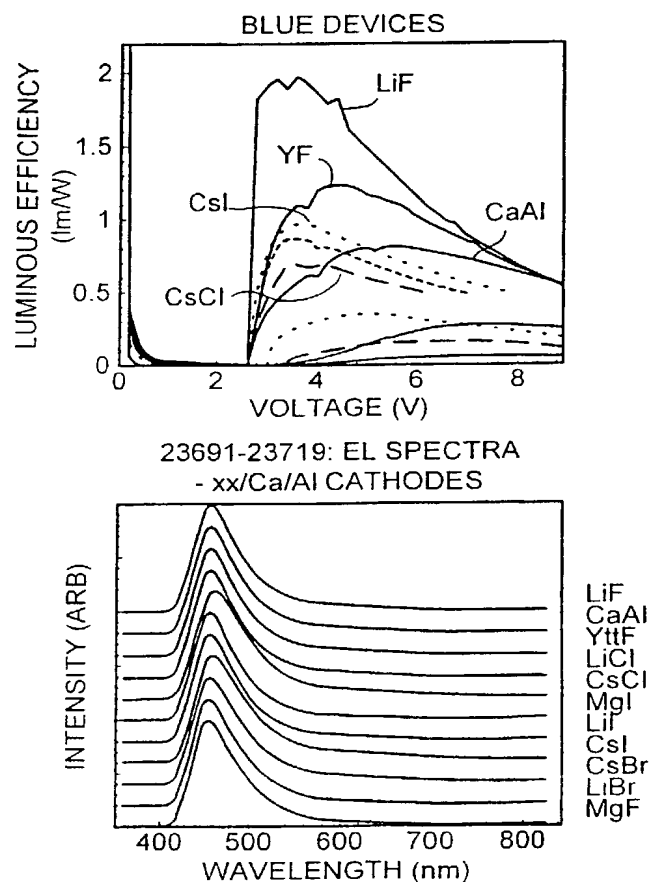


FIG. 5

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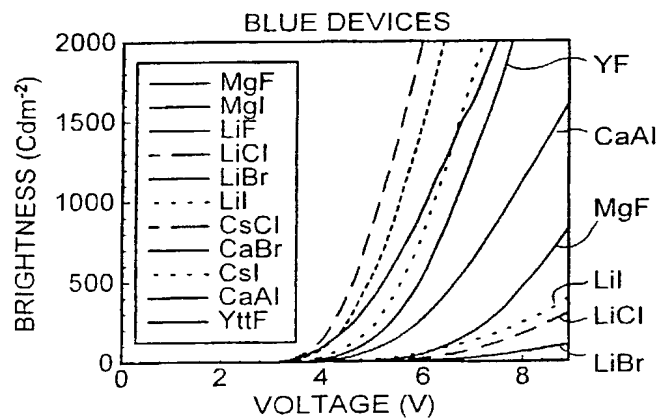
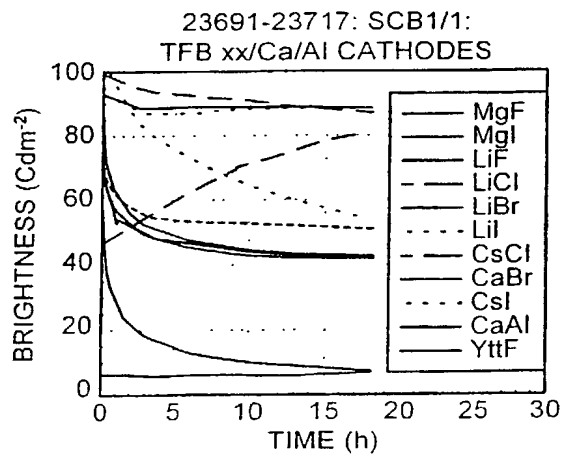
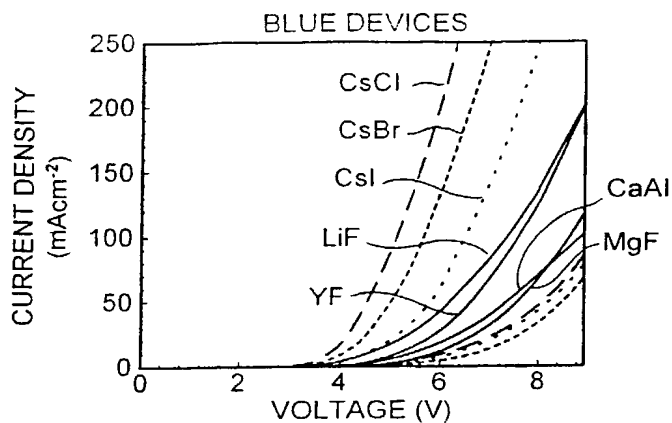


FIG. 5 CONT'D

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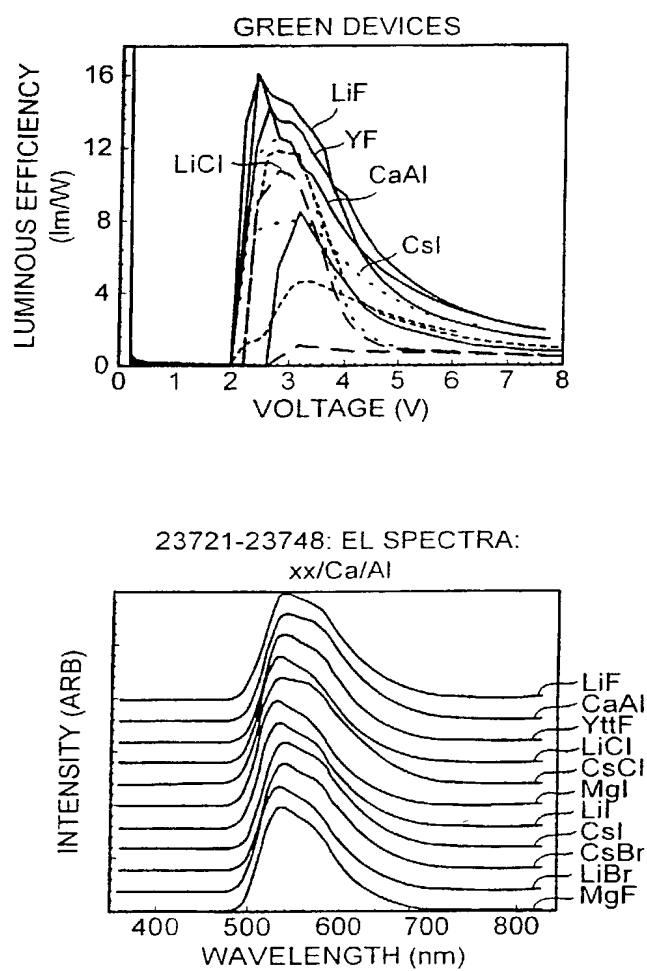


FIG. 6

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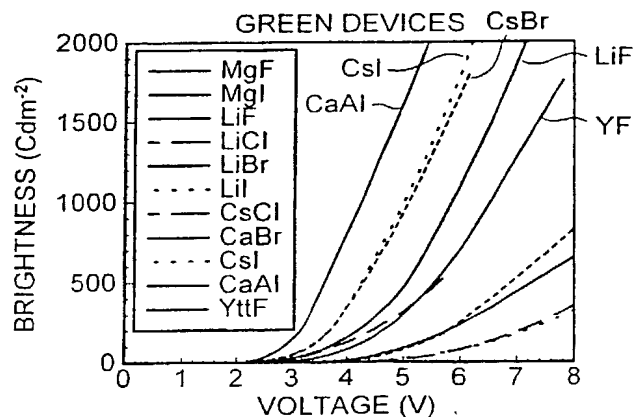
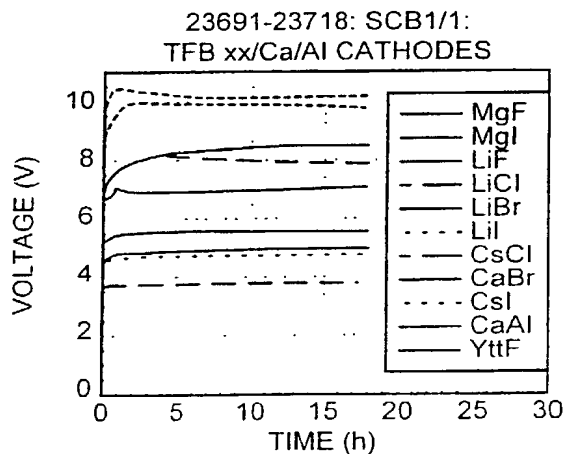
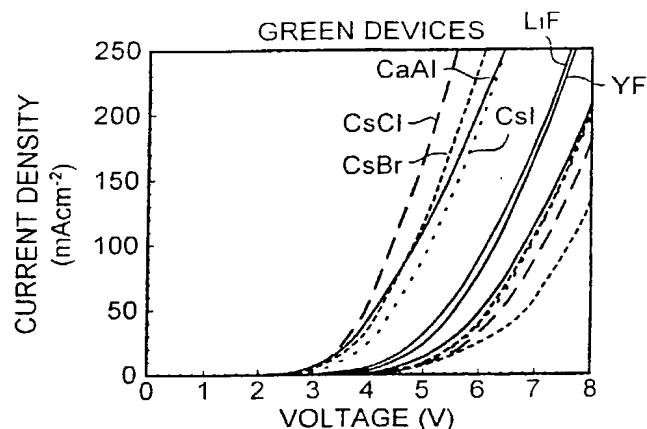


FIG. 6CONT'D

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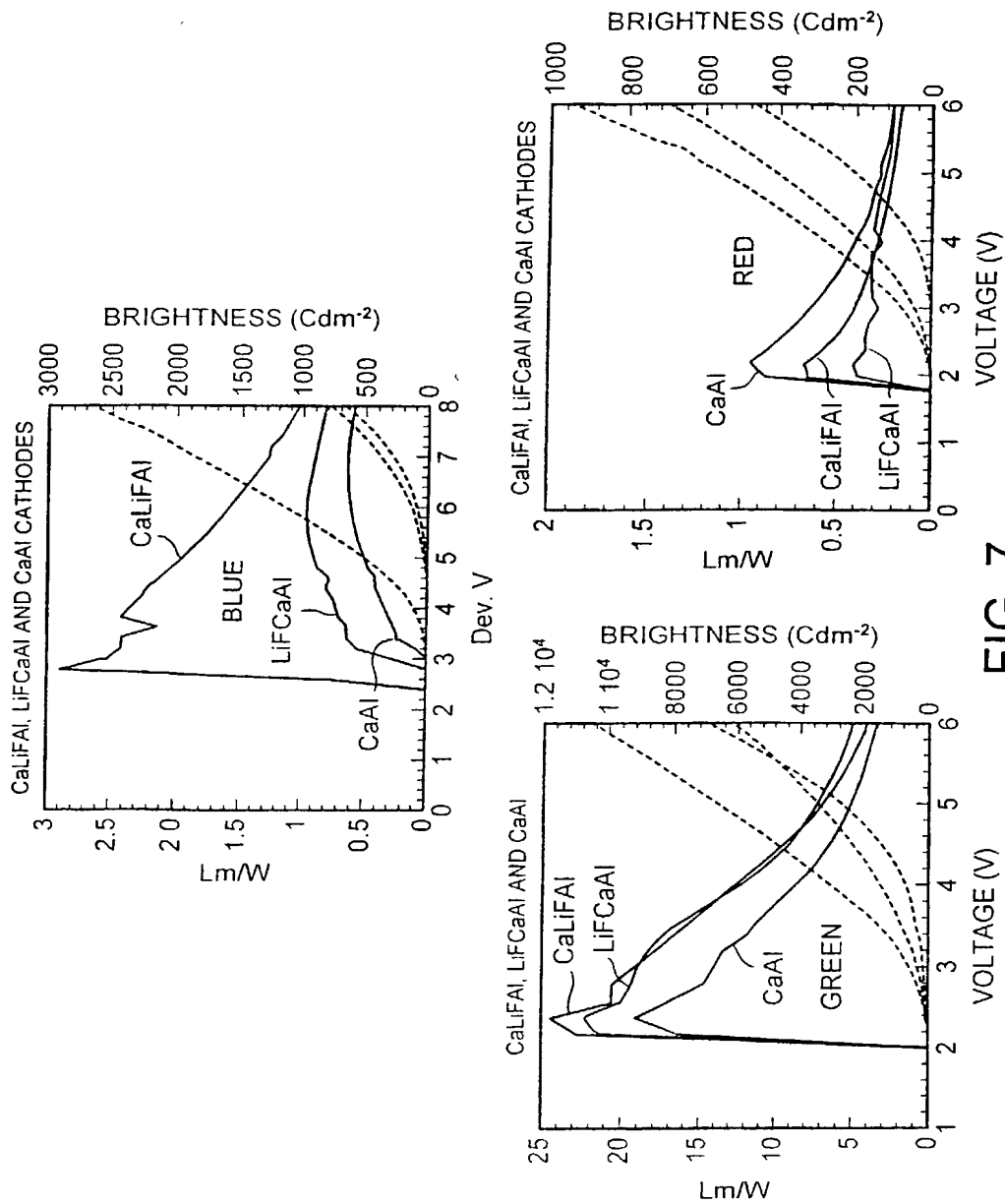


FIG. 7

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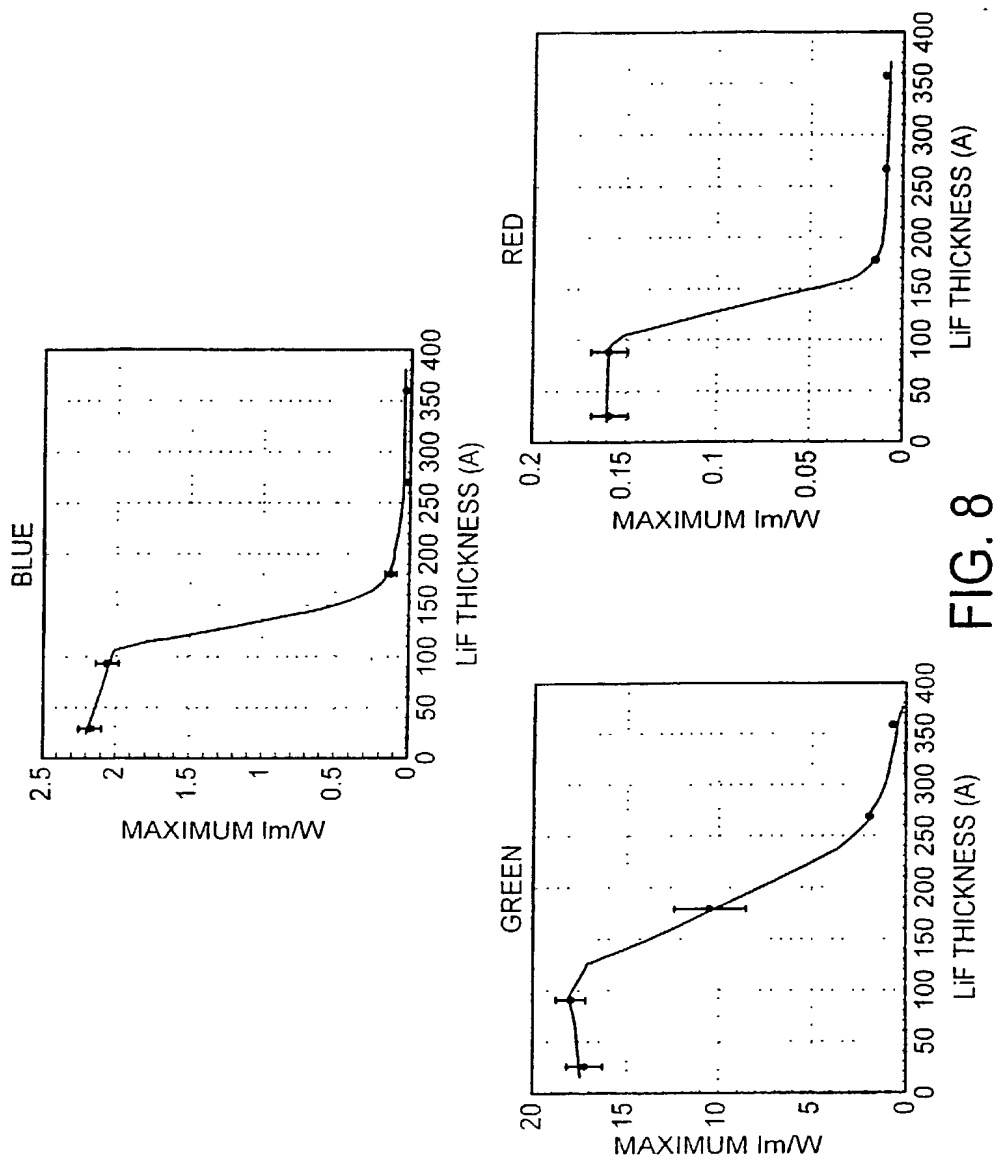


FIG. 8

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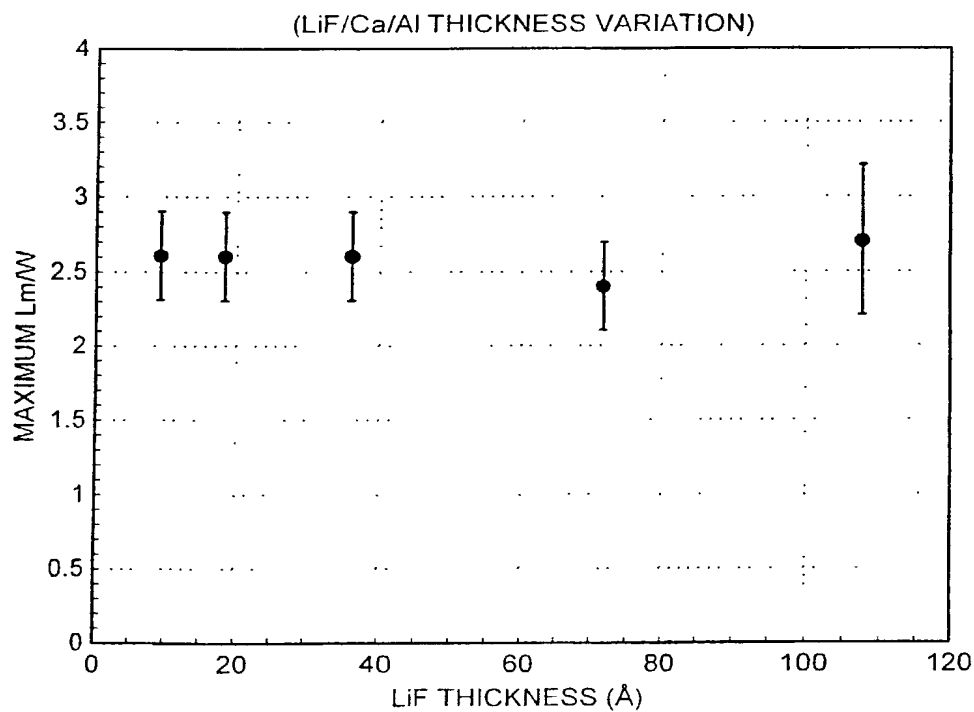


FIG. 9

DECLARATION FOR PATENT APPLICATION AND POWER OF ATTORNEY

As a below named inventor, I hereby declare that my residence, post office address and citizenship are as stated below next to my name; I believe that I am an original, first and joint inventor of the subject matter which is claimed and for which a patent is sought on the invention entitled "**OPTO-ELECTRICAL DEVICES**," the specification of which was filed on August 13, 2001, as Application Serial No. 09/913,381 and was amended on August 13, 2001. I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment(s) referred to above. I acknowledge the duty to disclose to the Patent and Trademark Office all information known to me to be material to patentability as defined in 37 C.F.R. §1.56.

I hereby claim foreign priority benefits under 35 U.S.C. §119 of any foreign application(s) for patent or inventor's certificate or of any PCT international application(s) designating at least one country other than the United States of America listed below and have also identified below any foreign application(s) for patent or inventor's certificate or any PCT international application(s) designating at least one country other than the United States of America filed by me on the same subject matter having a filing date before that of the application(s) of which priority is claimed:

Priority Claimed

9903251.8	Great Britain	12 February 1999	<input checked="" type="checkbox"/>	<input type="checkbox"/>
(Application Serial Number)	(Country)	(Day/Month/Year Filed)	Yes	No

I hereby claim the benefit under 35 U.S.C. §119(e) of any United States provisional application(s) listed below:

_____	_____
(Application Serial Number)	(Day/Month/Year Filed)

I hereby claim the benefit under 35 U.S.C. §120 of any United States application(s) or PCT international application(s) designating the United States of America listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior application(s) in the manner provided by the first paragraph of 35 U.S.C. §112, I acknowledge the duty to disclose to the Office all information known to me to be material to patentability as defined in 37 C.F.R. §1.56 which occurred between the filing date of the prior application(s) and the national or PCT international filing date of this application:

PCT/GB00/00476	14 February 2000	Pending
(Application Serial Number)	(Day/Month/Year Filed)	(Status-Patented, Pending or Abandoned)

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under 18 U.S.C. §1001 and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

APPLICABLE RULES AND STATUTES

37 CFR 1.56. DUTY OF DISCLOSURE - INFORMATION MATERIAL TO PATENTABILITY (Applicable Portion)

(a) A patent by its very nature is affected with a public interest. The public interest is best served, and the most effective patent examination occurs when, at the time an application is being examined, the Office is aware of and evaluates the teachings of all information material to patentability. Each individual associated with the filing and prosecution of a patent application has a duty of candor and good faith in dealing with the Office, which includes a duty to disclose to the Office all information known to that individual to be material to patentability as defined in this section. The duty to disclose information exists with respect to each pending claim until the claim is canceled or withdrawn from consideration, or the application becomes abandoned. Information material to the patentability of a claim that is canceled or withdrawn from consideration need not be submitted if the information is not material to the patentability of any claim remaining under consideration in the application. There is no duty to submit information which is not material to the patentability of any existing claim. The duty to disclose all information known to be material to patentability is deemed to be satisfied if all information known to be material to patentability of any claim issued in a patent was cited by the Office or submitted to the Office in the manner prescribed by §§ 1.97(b)-(d) and 1.98. However, no patent will be granted on an application in connection with which fraud on the Office was practiced or attempted or the duty of disclosure was violated through bad faith or intentional misconduct. The Office encourages applicants to carefully examine:

- (1) prior art cited in search reports of a foreign patent office in a counterpart application, and
- (2) the closest information over which individuals associated with the filing or prosecution of a patent application believe any pending claim patentability defines, to make sure that any material information contained therein is disclosed to the Office.

Information relating to the following factual situations enumerated in 35 USC 102 and 103 may be considered material under 37 CFR 1.56(a).

35 U.S.C. 102. CONDITIONS FOR PATENTABILITY: NOVELTY AND LOSS OF RIGHT TO PATENT

A person shall be entitled to a patent unless --

- (a) the invention was known or used by others in this country, or patented or described in a printed publication in this or a foreign country, before the invention thereof by the applicant for patent, or
- (b) the invention was patented or described in a printed publication in this or a foreign country or in public use or on sale in this country, more than one year prior to the date of the application for patent in the United States, or
- (c) he has abandoned the invention, or
- (d) the invention was first patented or caused to be patented, or was the subject of an inventor's certificate, by the applicant or his legal representatives or assigns in a foreign country prior to the date of the application for patent in this country on an application for patent or inventor's certificate filed more than twelve months before the filing of the application in the United States, or
- (e) the invention was described in a patent granted on an application for patent by another filed in the United States before the invention thereof by the applicant for patent, or on an international application by another who has fulfilled the requirements of paragraph (1), (2), and (4) of section 371(c) of this title before the invention thereof by the applicant for patent, or
- (f) he did not himself invent the subject matter sought to be patented, or
- (g) before the applicant's invention thereof the invention was made in this country by another who had not abandoned, suppressed, or concealed it. In determining priority of invention there shall be considered not only the respective dates of conception and reduction to practice of the invention, but also the reasonable diligence of one who was first to conceive and last to reduce to practice, from a time prior to conception by the other.

35 U.S.C. 103. CONDITIONS FOR PATENTABILITY; NON-OBVIOUS SUBJECT MATTER (Applicable Portion)

A patent may not be obtained though the invention is not identically disclosed or described as set forth in section 102 of this title, if the differences between the subject matter sought to be patented and the prior art are such that the subject matter as a whole would have been obvious at the time the invention was made to a person having ordinary skill in the art to which said subject matter pertains. Patentability shall not be negated by the manner in which the invention was made.

Subject matter developed by another person, which qualifies as prior art only under subsection (f) or (g) of section 102 of this title, shall not preclude patentability under this section where the subject matter and the claimed invention were, at the time the invention was made, owned by the same person or subject to an obligation of assignment to the same person.

35 U.S.C. 112. SPECIFICATION (Applicable Portion)

The specification shall contain a written description of the invention, and of the manner and process of making and using it, in such full, clear, concise, and exact terms as to enable any person skilled in the art to which it pertains, or with which it is most nearly connected, to make and use the same, and shall set forth the best mode contemplated by the inventor of carrying out his invention.

POWER OF ATTORNEY: I hereby appoint as my attorneys, with full powers of substitution and revocation, to prosecute this application and transact all business in the Patent and Trademark Office connected therewith:

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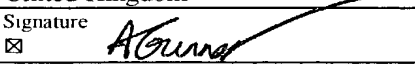
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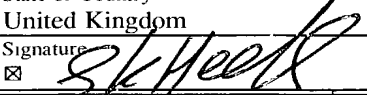
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State or Country United Kingdom	State or Country United Kingdom
Date <input checked="" type="checkbox"/>	Signature